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(54) **Combustible compositions containing gas oil, at least one fatty acid ester and an n-butane-base alcohol constituent which can be used in particular as diesel fuels**

(57) A combustible composition that is particularly suitable as a diesel fuel comprises from 10 to 60% by volume of at least one gas oil; from 10 to 60% by volume of at least one C_{1-8} alkyl ester of a C_{12-22} fatty acid; and from 10 to 50% by volume of a mixture containing at least *n*-butanol and acetone. The mixture may also contain 1 to 15% by weight of methanol. The ester in the composition may be prepared by transesterifying natural fatty materials. Cetane-number-improving additives may be added, especially when the cetane number would otherwise be below 40.

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SPECIFICATION

Combustible compositions containing gas oil, at least one fatty acid ester and an n-butanol-base alcohol constituent which can be used in particular as diesel fuels

The present invention concerns novel combustible compositions useful in particular as fuels for diesel engines, and which contain a gas oil, at least one fatty acid ester and a primarily alcohol constituent based on *n*-butanol and acetone.

We have already described and claimed the use as diesel fuels of primarily alcoholic constituents based on *n*-butanol mixed with gas oils, in French Patent Application No. EN 80/17147 for a first certificate of addition, filed on 1st August 1980, which is one of the priority documents on which our prior application No. 8117424 (published as Specification No. 2077290) is based.

This French application disclosed that the fuels or combustible materials for diesel engines could contain from 5 to 95% of gas oil and from 95 to 5% of one of the mixtures as defined above, the preferred proportions being from 75 to 90% of gas oil and from 25 to 10% of a mixture containing butanol and acetone.

In the specific Examples, the mixture used contained 75% of butanol and 25% of acetone, generally in a proportion of 20% for 80% of gas oil. With higher proportions (30 to 50%) of the butanol/acetone constituent, the cetane numbers of the mixtures formed with the gas oil could fall to values of less than 40, for example down to 30.

It has now been discovered that, with the highest proportions of primarily alcoholic constituent, for example from 30 to 50% by volume, it is possible to avoid an excessive drop in the cetane number, provided that a part of the gas oil is replaced by at least one fatty acid ester as defined hereinafter. The presence of such fatty acid esters in the combustible compositions according to the invention can also be advantageous with lower proportions of *n*-butanol-base alcohol constituent.

Thus, broadly, the combustible compositions according to the present invention, which can be used in particularly as fuels for diesel engines, comprise:

(a) from 10 to 60% by volume of at least one gas oil;
(b) from 10 to 60% by volume of at least one C_{1-8} alkyl ester of a C_{12-22} fatty acid,
(c) from 10 to 50% by volume of a primarily alcoholic constituent containing at least *n*-butanol and acetone.

If there is a requirement for combustible compositions having very high proportions of alcohol constituent, such compositions may comprise:

(a) from 10 to 40% by volume of at least one gas oil;
(b) from 30 to 60% by volume of at least one of the fatty acid esters; and
(c) from 30 to 50% by volume of the alcoholic constituent.

The primarily alcoholic constituents in accordance with the invention may contain:

n-butanol	from 40 to 85% by weight	Ia
acetone	from 15 to 60% by weight	

or

n-butanol	from 45 to 85% by weight	IIa
isopropanol	from 10 to 45% by weight	
acetone	from 1 to 25% by weight	

The various mixtures falling into the two categories indicated above may include proportions of ethanol, thus forming mixtures of the following types:

n-butanol	from 40 to 80% by weight	Ia
acetone	from 15 to 45% by weight	
ethanol	from 1 to 15% by weight	

and

n-butanol	from 45 to 75% by weight	IIb
isopropanol	from 10 to 40% by weight	
acetone	from 2 to 15% by weight	
ethanol	from 1 to 10% by weight	

Although the mainly alcoholic compositions based on *n*-butanol as defined above can be produced by simply mixing their various constituents, such compositions can also advantageously be produced by a fermentation process performed on a cellulosic substrate in the presence of at least one cellulolytic-enzyme-producing microorganism, operating either by acetone/butanol fermentation or by butanol/isopropanol fermentation, to give mixtures of the above-specified compositions.

For that purpose, it is possible to use any kinds of cellulosic substrates, for example those produced after pre-treatment of waste paper, cereal straw, bagasse, maize stalks or cobs, sawmill or lumber waste from deciduous or resinous woods. The pre-treatment in question may be mechanical (for example crushing or grinding) and/or chemical (for example treatment with sodium hydroxide, preferably with about 6% by weight of sodium hydroxide/weight of substrate).

Sugar hydrolysis (enzymatic reaction) is then carried out using the normal procedures, preferably at from 30 to 60°C, at a pH-value which is generally between 3.5 and 6.5, the operating conditions substantially depending on the nature of the micro-organism which is to be used in the subsequent stage.

Taking the resulting hydrolysates which are supplemented with nutrient elements, fermentation is carried out in the presence of organisms which are capable of producing cellulolytic enzymes. Such organisms are bacteria, preferably belonging to the genus *Clostridium* or fungi which preferably belong to the genera *Sporotrichum, Polyporus, Fusarium, Penicillium, Myrothecium* and *Trichoderma*. The fermentation operation which is performed anaerobically or aerobically is performed for example with a bacterium of the genus *Clostridium* at a temperature which is generally from 25 to 40°C, and with a pH-value which is generally between 4 and 7.5.

The factors which exert an influence on the composition of the mixtures produced are the strain used, the substrate and the fermentation conditions, that is to say, the pH-value, temperature, composition of the medium and in particular the nitrogen source.

The organisms used for the acetone/butanol fermentation process generally belong to the genus *Clostridium*. The species used have been described by the names *Clostridium saccharoacetobutylicium, Clostridium acetobutylicum, Clostridium saccharobutyl acetonicum,* and *Clostridium saccharoperbutylicum*. The type species is *Clostridium acetobutylicum*.

The organisms used for the butanol/isopropanol fermentation process, which are close to those indicated above, also belong to the genus *Clostridium*. The species used have been described by the names *Clostridium propylbutylicum* and *Clostridium viscifasciens,* but the type species used for this fermentation operation are *Clostridium butylicum* and *Clostridium beijerinckii* and *Clostridium toanum*.

Of the mixtures considered, use is most frequently made of mixtures containing from 40 to 85% by weight of n-butanol and from 60 to 15% by weight of acetone and more particularly again, mixtures containing approximately 75% by weight of n-butanol for 25% by weight of acetone, and mixtures containing about 60% by weight of n-butanol, 30% by weight of acetone and 10% by weight of ethanol.

The gas oils which are considered in accordance with the present invention are conventional gas oils, that is to say, cuts of petroleum origin which boil in a range of from 120—190°C to 300—380°C, with a mean molecular weight of around 200 (the molecular weight of the constituents of the gas oils can range from about 130 to about 250). They also have a variable proportion of aromatic hydrocarbons (for example from 20 to 35% by weight). Their kinematic viscosity at 20°C is generally a few centistokes, for example from about 4 to 9 cSt. They have a cetane number of the order of 38 to 58.

Such gas oils can be produced by the atmospheric distillation of crude oil or other refining operations such as cracking or hydrocracking.

The fatty acid esters used in the combustible compositions of the present invention generally comprise C_1 to C_8 alkyl esters of mono-carboxylic acids with a saturated or unsaturated aliphatic hydrocarbon chain, containing from 12 to 22 carbon atoms.

Examples of fatty acid esters that may be used include saturated acid esters such as methyl, ethyl, isopropyl, n-butyl, isooctyl or 2-ethylhexyl laurates (C_{12}), myristates (C_{14}), palmitates (C_{16}) and stearates (C_{18}), which can be used alone or in the form of mixtures with each other and unsaturated fatty acid esters such as methyl, ethyl, isopropyl, n-butyl, isooctyl or 2-ethylhexyl lauroleates (C_{12}), myristoleates (C_{14}), palmitoleates (C_{16}), oleates and linoleates (C_{18}), gadoleates (C_{20}) and erucates (C_{22}), which are used alone or as mixtures with each other.

It is also possible to use fatty acid esters derived from natural fatty substances, oils or greases, of vegetable or animal origin. In this respect, examples of oils of vegetable origin that may be mentioned include copra oils and coconut oils (in particular babassu coconut oil), the "acid part" of which contains

substantial proportions of saturated fatty acids (primarily lauric acid, myristic and/or palmitic acid); other examples of oils of vegetable origin are colza, sunflower, soya, maize, cotton, almond, peanut, olive, palm or palm cabbage oils, the "acid part" of which contains substantial proportions of unsaturated fatty acids (primarily oleic acid and/or linoleic acid).

Mention may also be made of castor oil (in particular mamona oil) and linseed oil. However, the degree of unsaturation of the last two is much too high to produce alkyl esters that can be used as diesel fuel constituents. In order to be able to use such oils, they have to be stabilised, by submitting them to preliminary partial hydrogenation.

Lard and tallow may be mentioned as examples of fatty substances of animal origin.

The esters derived from copra oil, coconut oil (in particular babassu coconut oil), palm oil (in particular, Dendé palm oil), or cotton oil will be more particularly considered in accordance with the invention.

The following Table shows the main fatty acids which constitute the "acid part" of the above-mentioned oils:

Oil of / acid % weight	Copra	Coconut	Palm	Cotton
Lauric	48	48	–	–
Myristic	18	17.5	–	–
Palmitic	10	9	42.5	21
Oleic	–	6	43	33
Linoleic	–	–	9.5	43.5

The fatty acid esters which are used in accordance with the invention can be prepared from fatty acids themselves when they are readily available. In that case, operation is by simple esterification by means of the appropriate C_1 to C_8 alcohol (for example, methanol, ethanol, isopropanol, n-butanol, isooctanol or 2-ethylhexanol), using any normal method.

They may also be prepared by transesterification from esters in which the "alcohol" part derives from alcohols other than those considered in accordance with the invention. It is in this way in particular that operation is effected when the raw materials to be used are natural fatty substances (oils or greases of vegetable or animal origin) which comprise mixtures of glyceric esters of various saturated or unsaturated fatty acids. The fatty substances which are advantageously used in this way are those in which the "acid" part contains substantial proportions of saturated or unsaturated-chain fatty acids, such as the various oils referred to above.

In order to produce the esters or mixtures of esters required, transesterification is carried out by means of methanol (for example using the method disclosed in US patent No 2 360 844) or other suitable alcohols such as for example ethanol, isopropanol, n-butanol, isooctanol or 2-ethylhexanol, according to circumstances.

Without departing from the scope of the invention, it is also possible to use unsaturated fatty acid esters or mixtures of unsaturated fatty acid esters, which have been partially hydrogenated, using the normal methods of selective hydrogenation.

The combustible compositions as defined hereinbefore generally have a cetane number of the order of 40 or higher, suitable viscosities for use as diesel fuels, and good characteristics in the cold condition.

It may happen nonethless that some of these compositions, in particular those which have the highest proportion of n-butanol-base alcohol constituent, have cetane numbers which are a little lower. In that case, it is possible to add to such compositions, conventional cetane number improving additives such as alkyl nitrates (for example amyl nitrate, hexyl nitrate or octyl nitrate), in sufficient proportions, for example from 0.1 to 2% by weight, to raise the cetane number to a value of at least 40.

Moreover, when they are used as fuels for diesel engines, various conventional additives which are compatible with the fatty acid esters used may be added to the compositions of the invention. Thus, it may be desirable for anti-oxidising additives to be incorporated in such compositions. Additives for improving cold characteristics, anti-smoke additives, etc., may also be added to the compositions.

The following Examples illustrate the invention and are in no way to be considered as limiting.

EXAMPLE A

Compositions 1 to 11

Various mixtures according to the invention were produced, containing a gas oil, a n-butanol-base alcohol constituent and a fatty acid ester.

The gas oil used has the following main characteristics:

Specific gravity at 20°C:	0.828
Viscosity at 20°C	: 4.16 cSt
Cloud point	: –2°C
Pour point	:–18°C
Filtrability limit temperature	: –8°C
Distillation range	: 167—359°C
Aromatics content	: 24%
Cetane number	: 54

The alcohol constituent contains 75% by weight of n-butanol an 25% by weight of acetone (it will be referred to hereinafter by means of the designation MBA).

In one of the mixtures according to the invention (indicated as No. 4), the fatty acid ester comprises a mixture of methyl esters, derived by alcoholysis of copra oil using methanol (the acid part of copra oil primarily contains about 48% of lauric acid, about 18% of myristic acid and about 10% of palmitic acid).

The proportions of the various constituents of the mixtures according to the invention and the cetane numbers thereof are set out in the following Table (Table I).

The cold characteristics (cloud point and pour point) have been set forth in relation to some of those mixtures.

TABLE I

Ref. No.	Gas Oil % Vol	Fatty acid ester nature	% Vol	MBA % Vol	Cetane number	Cloud point (°C)	Pour point (°C)
1	55	methyl oleate (1)	15	30	38.0 (*)		
2	50	methyl oleate (2)	20	30	38.0 (*)		
3	20	methyl oleate (1)	40	40	40.6	–6	–18
4	30	copra methyl esters	30	40	34.9 (*)		
5	20	isopropyl myristate	40	40	40.6	–7	–13
6	30	methyl palmitate	30	40	39.3		
7	20	methyl stearate	40	40	40.9	+25	+21
8	30	n-butyl stearate	30	40	38.5 (*)		
9	20	n-butyl stearate	40	40	39.3	+9	+3
10	30	isooctyl stearate	30	40	37.0 (*)		
11	20	isooctyl stearate	40	40	39.0	+3	–3

(1) (2) two different commercial batches of methyl oleate were used.

(*) In the case of these mixtures, the addition of small amounts of amyl nitrate (0.1 to 2% by weight, depending on the case involved) made it possible to raise the cetane number to a value of 40 or slightly above.

EXAMPLE B

Compositions 12 to 15

Other ternary mixtures were also produced, of (a) methyl esters of vegetable origin, (b) a gas oil with a cetane number of 54 and (c) an alcohol constituent consisting of a mixture of n-butanol (75% by weight), and acetone (25% by weight) (referred to as MBA).

The composition of these mixtures and their cetane number are set out in Table II below:

TABLE II

Ref. No.	Methyl esters	% Vol	Gas oil (% vol)	M B A (% vol)	Cetane number
12	coconut oil (babassu)	25	35	40	40.1
13	coconut oil (babassu)	35	25	40	41.8
14	palm oil (Dendé palm)	30	35	35	39.5 (*)
15	cotton oil	20	50	30	39.4 (*)

(*) In the case of these mixtures, the addition of 0.5% by weight of amyl nitrate enabled the cetane number to be raised to a value of 40 or slightly higher.

TESTS ON A DIESEL ENGINE

Some compositions of the invention were tested on an agricultural tractor diesel engine (speed of 2400 r.p.m.), for a period of 50 hours for each composition.

The compositions tested were mixtures Nos. 3 and 5 as set forth in Table I above, and mixture No. 13 set forth in Table II.

These tests did not result in any trouble or breakdown. No deposit at the injectors was found. Moreover, it was found that the power output of the engine was maintained at a normal level.

CLAIMS

1. A combustible composition comprising:

(a) from 10 to 60% by volume of at least one gas oil;
(b) from 10 to 60% by volume of at least on C_{1-8} alkyl ester of a C_{12-22} fatty acid; and
(c) from 10 to 50% by volume of a mixture containing at least *n*-butanol and acetone.

2. A composition according to Claim 1 comprising:

(a) from 10 to 40% by volume of at least one gas oil;
(b) from 30 to 60% by volume of at least one of the alkyl esters of fatty acids; and
(c) from 30 to 50% by volume of the mixture containing at least *n*-butanol and acetone.

3. A composition according to Claim 1 or 2 in which mixture (c) contains from 40 to 85% by weight of *n*-butanol and from 15 to 60% by weight of acetone.

4. A composition according to Claim 3 in which mixture (c) further contains from 1 to 15% by weight of ethanol.

5. A composition according to Claim 1 or 2 in which mixture (c) contains from 45 to 85% by weight of *n*-butanol, from 10 to 45% by weight of isopropanol, and from 1 to 25% by weight of acetone.

6. A composition according to Claim 5 in which mixture (c) further contains from 1 to 10% by weight of ethanol.

7. A composition according to Claim 3 in which mixture (c) contains approximately 75% by weight of *n*-butanol and 25% by weight of acetone.

8. A composition according to Claim 4 in which mixture (c) contains about 60% by weight of *n*-butanol, 30% by weight of acetone and 10% by weight of ethanol.

9. A composition according to any one of Claims 1 to 8 in which the fatty acid ester (b) is isopropyl myristate, methyl palmitate, methyl stearate, *n*-butyl stearate, isooctyl stearate or methyl oleate.

10. A composition according to any one of Claims 1 to 9 in which the fatty acid ester (b) comprises a mixture of esters derived from colza, sunflower, soya, maize, cotton, almond, peanut, olive, palm, palm cabbage, coconut or copra oil.

11. A composition according to Claim 10 in which the fatty acid ester (b) comprises a mixture of methyl esters derived from copra oil, coconut oil, palm oil or cotton oil.

12. A composition according to any one of Claims 1 to 11 having a cetane number of at least 40.

13. A composition according to any one of Claims 1 to 11 further comprising a proportion of cetane-number-improving additive sufficient to give a cetane number of at least 40.

14. A composition according to any one of Claims 1 to 13 further comprising a suitable proportion of at least one antioxidant.

15. A composition according to Claim 1, substantially as hereinbefore described in any one of the Examples.

16. A composition according to any one of Claims 1 to 15 for use as a fuel for supplying a diesel engine.

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